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Project Summary

Field Test of a Generic Method For Halogenated Hydrocarbons: A VOST Test at a Chemical Manufacturing Facility

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Laboratory evaluation studies were performed for the volatile halogenated organic compounds (VHOCs) listed in Title III of the Clean Air Act Amendments (CAAA) of 1990 to determine chromatographic retention times, recoveries from sorbent, and method detection limits, as well as to design (where necessary), construct, and evaluate dynamic spiking equipment and procedures for VOST. An initial field evaluation study was conducted for the VOST (SW-846 sampling Method 0030, analytical Method 5041) with dynamic spiking of VHOCs. A chemical manufacturing facility was selected as a second test site. The presence of low levels of some of the compounds of interest was established by the VOST analysis of samples collected during a presurvey. For the field evaluation study, quadruple trains were operated from 4 collocated sampling probes, with 2 dynamically-spiked trains and 2 unspiked trains. A sampling scheme to meet the requirements of method evaluation was designed statistically (following the guidelines for EPA Method 301), and the data were evaluated statistically. Of 23 VHOCs tested, the VOST showed acceptable performance with respect to recovery and precision for 17.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The validation of a method for a particular analyte or group of analytes means that the performance of the methodology for these analytes has been established and demonstrated through field tests at the type of source category of interest, and that the precision and bias of the method have been established experimentally. The U. S. EPA, under the authority of Title III of the CAAA of 1990, required the identification and/or validation of sampling and analytical methods for the VHOCs listed in Table 1. The candidate method is VOST, which consists of SW-846 Sampling Method 0030 and SW-846 Analytical Method 5040 or 5041. EPA determined that the VOST method should first be evaluated in a laboratory environment to establish the veracity of the spiking procedure and the potential applicability of the analytical procedures for the compounds listed in Table 1.

The VOST was evaluated at a coal-fired power plant using quadruple VOST trains sampling from 4 collocated sampling probes to provide further verification of the dynamic spiking methodology in a non-laboratory environment and to assess the added effect of sampling a combustion matrix upon the performance of the methodology. Data obtained in the first field evaluation showed that the VOST did not perform acceptably for all of the candidate analytes. The methodology was not expected to show acceptable performance for all of the candidate analytes listed in Table 1, but all of the candidate analytes were included in the testing to demonstrate definitively when the methodology

would not perform well and to provide quantitative data to assess method performance. Three of the candidate analytes could not be analyzed by the VOST analytical methodology: epichlorohydrin, bis(chloromethyl) ether, and chloromethyl methyl ether. These 3 compounds are polar, water-soluble, and very reactive, so they either could not be purged from the water or reacted with the water.

A second field evaluation study was conducted at a chemical manufacturing facility where chemical waste was incinerated. Dynamic spiking of the analytes listed in Table1 was performed, using 4 collocated sampling probes with 4 similar VOST trains. The guidelines of EPA Method 301 were used to design the sampling strategy to ensure that adequate samples were available for statistical evaluation of bias and precision.

Procedure

The objective of this program was to perform a second field evaluation of the VOST method (sampling method SW-846 Method 0030; analytical method, SW-846 Method 5041) at a chemical manufacturing facility that incinerated chemical waste, to allow the collection of sufficient data to be able to establish the bias and precision of the method for the VHOCs listed in Title III of the CAAA of 1990.

To achieve this objective, a field test site was selected to allow access for the quadruple sampling trains required for testing, with 4 collocated sampling probes. Collection and evaluation of the data followed one of the acceptable approaches detailed in EPA Method 301: dynamic analyte spiking. The criteria for acceptable performance of the method for an analyte are recovery within the range of 50% to 150% with precision (expressed as percent relative standard deviation of replicate determinations) of 50 or less.

Sampling was performed by withdrawing gas from a single port in the stack through a Quad probe, then directing the sampled gas simultaneously to 4 similar VOST sampling trains. The Quad probe consists of 4 heated probes that can be inserted into the stack as one unit. The front end of the Quad probe was positioned in the center of the stack and remained in that location during each day of testing. No traverse of the stack was performed with the Quad probe. The true concentrations of the components of the stack gas were of no interest to this program as long as any quantities of the compounds of interest were equal for each train. For VOST sampling during the field evaluation, two of the trains of each Quad run were dynamically spiked and two were unspiked. Sampling procedures followed Method 0030.

Dynamic spiking of candidate VOST compounds was performed using a compressed gas cylinder containing the VHOCs. The boiling point maximum of 100°C cited in Method 0030 was extended to approximately 135°C to include chlorobenzene and ethylene dibromide, compounds frequently determined by the VOST methodology. The apparatus shown in Figure 1 was used for dynamic spiking in the field, with the spiking gas allowed to flow through the spiking apparatus for 2 hr before directing the flow to the sampling trains to minimize any adsorptive

Table 1. *Halogenated Compounds for Which Laboratory Testing has Determined the Applicability of the VOST Method*

Compound	*Boiling point (°C)*	*Comments*
allyl chloride	*44-46*	*Acceptable performance in laboratory*
bis(chloromethyl) ether	*106*[1]	*Decomposes in water; cannot be analyzed*
carbon tetrachloride	*77*	*Recovery too high in laboratory study*
chlorobenzene	*132*[1]	*Acceptable performance in laboratory*
chloroform	*60.6-61.5*	*Acceptable performance in laboratory*
chloromethyl methyl ether	*55-57*	*Decomposes in water; cannot be analyzed*
chloroprene	*59.4*	*Acceptable performance in laboratory*
1,3-dichloropropylene	*105-106*[2]	*Acceptable performance in laboratory*
epichlorohydrin	*115-177*[1]	*Decomposes in water; cannot be analyzed*
ethyl chloride (chloroethane)	*12*[3]	*Acceptable performance in laboratory*
ethylene dichloride (1,2-dibromoethane)	*131-132*[1]	*Acceptable performance in laboratory*
ethylidene dichloride (1,2-dichloroethane)	*83*	*Acceptable performance in laboratory*
methyl bromide (bromomethane)	*4*[3]	*Recovery unacceptably high in laboratory*
methyl chloride (chloromethane)	*-24.2*[3]	*Erratic and unacceptable in laboratory*
methyl chloroform (1,1,1-trichloroethane)	*74-76*	*Recovery too high in laboratory study*
methylene chloride	*39.8-40*	*Recovery too high in laboratory study*
methyl iodide (iodomethane)	*41-43*	*Acceptable performance in laboratory*
propylene dichloride (1,2-dichloropropane)	*95-96*	*Acceptable performance in laboratory*
tetrachloroethylene	*121*[1]	*Acceptable performance in laboratory*
1,1,2-trichloroethane	*110-115*[1]	*Acceptable performance in laboratory*
trichloroethylene	*86.9*	*Acceptable performance in laboratory*
vinyl chloride	*-13.4*[3]	*Acceptable performance in laboratory*
vinyl bromide	*16*[4]	*Acceptable performance in laboratory*
vinylidene chloride (1,1-dichloroethylene)	*30-32*	*Acceptable performance in laboratory*

[1] Above the maximum VOST boiling point of 100°C; included in the testing because compounds in the range of 100-132°C are frequently tested by the VOST method.
[2] Boiling temperature at 730 mm Hg.
[3] Below the common lower temperature limit of 30°C usually used for VOST.
[4] Boiling temperature at 750 mm Hg.

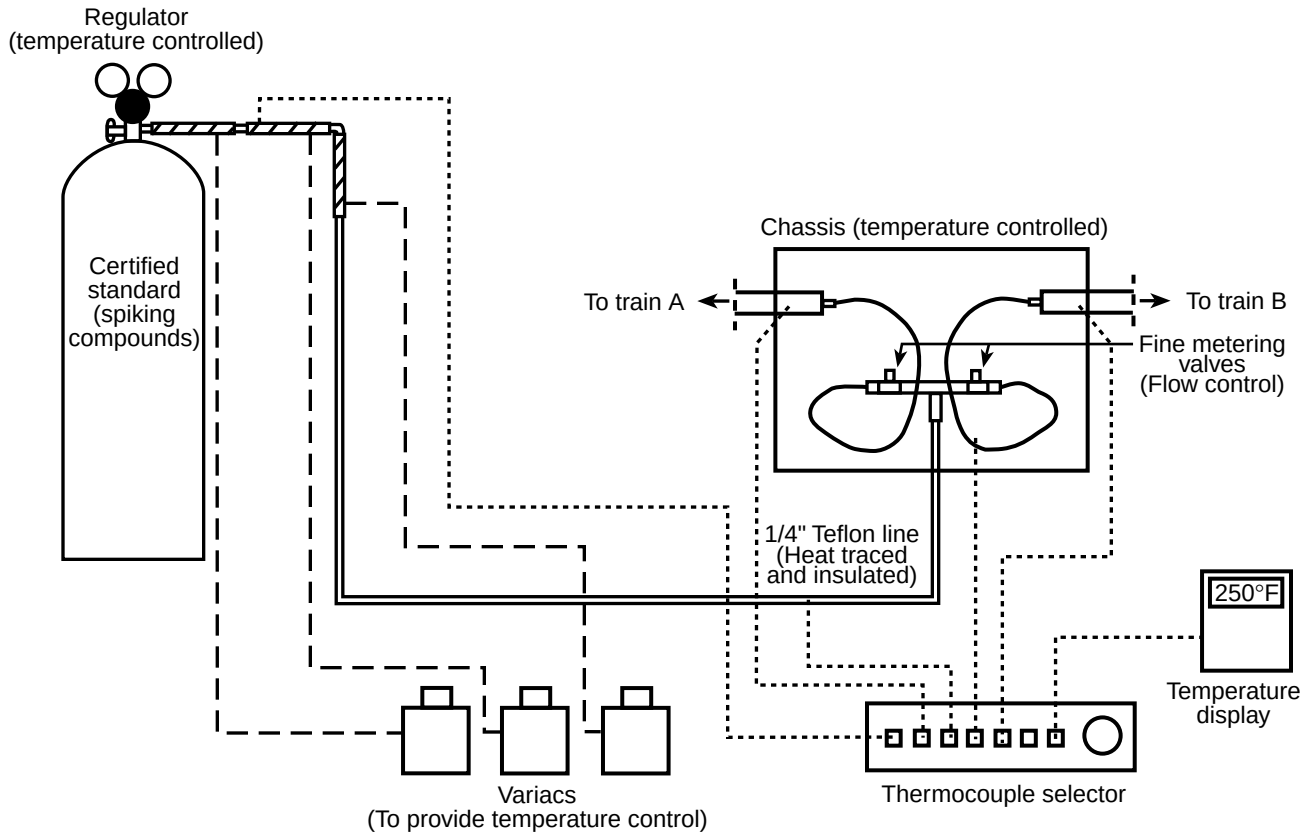

Figure 1. *VOST spiking apparatus.*

losses in the sampling trains. The concentration of compounds in the cylinder was verified by laboratory GC/MS and GC/multiple detector analysis of a diluted sample prepared in a SUMMA®*-polished canister.

Analysis of field samples was performed according to SW-846 Method 5041, analyzing each tube individually to establish distribution of compounds. A total of 6 complete and valid Quad runs (24 Tenax®/Tenax®-charcoal pairs, 12 spiked, 12 unspiked) is required to satisfy the requirements of the field validation protocol. However, a total of 10 Quad runs was performed to provide back-up samples in the event that any samples became invalid due to breakage or loss during analysis. The 2 tubes associated with each sample pair were analyzed separately, always analyzing the Tenax®-charcoal tube first to minimize the possibility of carryover from the front tube, where higher compound concentrations were expected. All VOST sampling tubes were transported and stored at 4°C and were analyzed within 30 days after collection.

Results and Discussion

The complete analytical results for each sampling train, showing recoveries of dynamically-spiked compounds and of surrogate compounds for the front and back tubes individually are shown in Appendix A of the project report. No corrections were performed for background concentrations because analyte concentrations in the background samples were less than five times the Method Detection Limit. Mean analyte recoveries and precision for 6 sampling runs are summarized in Table 2.

The results for the first and second VOST field evaluation studies are compared in Table 3. Using the criteria for acceptable performance of recovery between 50 and 150%, with precision (as expressed by relative standard deviation) of 50 or less, acceptable performance of the VOST methodology for a given compound is indicated in Table 3 by an asterisk.

Methyl chloride exhibited recoveries far above the acceptable range, consistent with results obtained in previous studies. The common factor in the excessive recoveries for methyl chloride appears to be formation of the compound in the time that the halogenated organic compounds are adsorbed on the sorbent tubes. Method 8240 shows acceptable and reproducible performance for methyl chloride, but sorbent residence times are minimal in this analytical methodology. Where sorbent residence time is minimal (e.g., spiked sorbent tubes are analyzed immediately), recoveries are within the reasonable range, although somewhat high. When methyl chloride and other halogenated compounds are retained on the sorbent for a period of days, excessive values for methyl chloride recovery are observed. Analytical results for methyl chloride using the VOST methodology are biased high, frequently by a factor of ten or more.

Analyte distribution is summarized in Table 4. As expected, methyl chloride, ethyl chloride, methyl bromide, and vinyl chloride are found almost exclusively on the back tube, because these compounds break through Tenax® very readily. However, methyl bromide and ethyl chloride

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table 2. *Summary of Mean Recovery and Precision for 6 VOST Sampling Runs Using Dynamic Spiking*

Compound	Average recovery (%)	% RSD
Recovery 50-150%—Precision ≤ 50% Relative Standard Deviation (RSD)		
propylene dichloride (1,2-dichloropropane)	*121*	*24.8*
trichloroethylene	*119*	*26.2*
chloroform	*91.3*	*31.1*
methyl chloroform (1,1,1-trichloroethane)	*91.1*	*24.6*
methylene chloride	*89.9*	*14.3*
ethylidene dichloride (1,1-dichloroethane)	*82.2*	*23.3*
chlorobenzene	*81.2*	*22.1*
carbon tetrachloride	*81.2*	*23.6*
1,1,2-trichloroethane	*79.7*	*27.2*
ethylene dibromide (1,2-dibromoethane)	*79.6*	*37.4*
cis-1,3-dichloropropene	*79.5*	*27.6*
vinylidene chloride (1,1-dichloroethylene)	*77.8*	*24.2*
chloroprene	*72.4*	*23.0*
ethylene dichloride (1,2-dichloroethane)	*72.3*	*37.5*
tetrachloroethene	*60.1*	*27.9*
methyl bromide (bromomethane)	*54.8*	*26.2*
trans-1,3-dichloropropene	*52.3*	*35.4*
Acceptable recovery, unacceptable precision		
methyl iodide (iodomethane)	*79.5*	*63.1*
Unacceptable recovery (low), acceptable precision		
vinyl chloride	*41.8*	*44.6*
allyl chloride (3-chloropropene)	*35.6*	*33.3*
ethyl chloride (chloroethane)	*33.7*	*36.9*
vinyl bromide	*29.8*	*29.7*
Unacceptable recovery (high), unacceptable precision		
methyl chloride (chloromethane)	*243*	*62.8*

frequently show an approximately even distribution between the front tube and the back tube. Other compounds are distributed between the front tube and back tube, with the highest compound concentration on the front tube. Highly halogenated compounds such as methylene chloride, carbon tetrachloride, and methyl chloroform show a distribution between front and back tubes, but with a clear predominance on the front tube. Using the criterion of 30% distribution on the back tube as an indicator of breakthrough (*Handbook: Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration,* EPA/625/6-89/023, January, 1990), no breakthrough was observed for any compound.

Conclusions

The following conclusions can be drawn from the data obtained in VOST field evaluation:

- The VOST method performed acceptably for the majority of the candidate VHOCs in 2 field tests. The VOST methodology showed unacceptable performance for only 2 compounds in both field evaluation studies: methyl chloride and allyl chloride.
- The VOST method performed acceptably for the following compounds in only 1 field evaluation: vinyl chloride, ethyl chloride, vinyl bromide, ethylene dibromide, and chloroprene. The success of the methodology for these analytes is source-dependent.
- Vinyl chloride, allyl chloride, chloroprene, and vinyl bromide all show marginal or unsuccessful performance in the VOST methodology. The presence of the double-bond in the analyte molecule appears to significantly decrease the probability of successful performance of the VOST method.

On the basis of laboratory and field evaluation studies for the VHOCs from Title III of the CAAA of 1990, the following recommendations are made:

- Consideration of the chemical properties of the compounds which were not amenable to the VOST analytical methodology (epichlorohydrin, chloromethyl methyl ether, bis[chloromethyl] ether) predicts that successful performance is very unlikely. These compounds are reactive, polar, and water-soluble. A method other than the VOST will be required for the successful sampling and analysis of these types of compounds.
- Methyl chloride has demonstrated excessively high values for recoveries in two field evaluation studies, as well as in laboratory studies. Because of this high bias, the VOST is not recommended as a sampling and analytical method for this compound.
- Further study of the VOST should be performed and/or VOST data should be collected in order to set appropriate recovery limits for the surrogates recommended in the analytical method. At present, the surrogates can only be used qualitatively: poor surrogate recoveries indicate problems with the matrix or the methodology.
- Modification or replacement of the VOST methodology should be investigated to provide a feasible sampling and analytical method for the volatile, polar, water-soluble compounds listed in Title III of the CAAA of 1990.

Table 3. *Comparison of Results for First and Second VOST Field Evaluations*

Compound	First field test [1]		Second field test [1]	
	Recovery(%)	RSD (%)	Recovery (%)	RSD (%)
methyl chloride	937	53.8	243	62.8
ethylidene dichloride	75.7*	13.7	82.2*	23.3
chlorobenzene	88.2*	22.0	81.2*	22.1
vinyl chloride	110.4*	27.3	41.8	44.6
vinylidene chloride (1,1-dichloroethylene)	88.0*	31.3	77.8*	24.2
chloroform	81.8*	14.8	91.3*	24.6
propylene dichloride (1,2-dichloropropane)	67.2*	9.6	121*	24.8
methyl bromide (bromomethane)	53.7*	20.2	54.8*	26.2
ethyl chloride (chloroethane)	50.3*	28.7	33.7	36.9
methylene chloride	77.7*	27.1	89.9*	14.3
methyl chloroform (1,1,1-trichloroethane)	110*	43.5	91.1*	31.1
carbon tetrachloride	107*	47.2	81.2*	23.6
ethylene dichloride (1,2-dichloroethane)	76.6*	33.0	72.3*	37.5
trichloroethylene	126*	15.6	119*	26.2
cis-1,3-dichloropropene	137*	26.0	79.5*	27.6
trans-1,3-dichloropropene	135*	38.1	52.3*	35.4
1,1,2-trichloroethane	98.0*	22.1	79.7*	27.2
tetrachloroethene	97.7*	21.9	60.1*	27.9
methyl iodide (iodomethane)	72.8*	37.6	79.5	63.1
allyl chloride (3-chloropropene)	29.9	19.5	35.6	33.3
ethylene dibromide (1,2-dibromoethane)	34.9	31.6	79.6*	37.4
chloroprene	40.1	22.4	72.4*	23.0
vinyl bromide	60.7*	34.3	29.8	29.7

Chloromethyl methyl ether, bix(chloromethyl) ether, and epichlorohydrin could not be analyzed by the VOST methodology.
* Acceptable performance by the analyte in the VOST method, using acceptability criteria of 50-150% recovery with percent Relative Standard Deviation (RSD) of 50 or less.
[1] Mean of 6 runs (twelve pairs) uncorrected for background.

Table 4. *Distribution Between Front and Back Tubes According to Compound*

Compound	Average recover (front)	Average recovery (back)
Compounds recovered on the front tube (≥ 90% on front tube)		
cis-1,3-dichloropropene	100.0	0.0
trans-1,3-dichloropropene	99.9	0.1
ethylene dichloride (1,2-dibromoethane)	99.9	0.1
trichloroethene	99.7	0.3
tetrachloroethene	99.6	0.4
chlorobenzene	99.5	0.5
propylene dichloride (1,2-dichloropropane)	99.5	0.5
chloroprene	99.0	1.0
1,1,2-trichloroethane	97.7	2.3
ethylene dichloride (1,1-dichloroethane)	96.8	3.2
chloroform	95.8	4.2
allyl chloride (3-chloropropene)	93.7	6.3
methyl iodide (iodomethane)	93.2	6.8
ethylene dichloride (1,2-dichloroethane)	92.0	8.0
Compounds distributed between front and back tubes		
methyl chloride (chloromethane)	16.5	83.5
vinyl chloride	19.3	80.7
methyl bromide (bromomethane)	36.5	63.5
chloroethane	55.1	44.9
vinyl bromide	73.2	26.8
methylene chloride (chloromethane)	81.7	18.3
carbon tetrachloride	84.5	15.5
methyl chloroform (1,1,1-trichloroethane)	86.3	13.7

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The complete report, entitled "Field Test of a Generic Method for Halogenated Hydrocarbons: A VOST Test at a Chemical Manufacturing Facility," (Order No. PB95-129144/AS; Cost: $19.50, subject to change) will be available only from:
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